Notes

Determination of the Nucleophilicities of N,N-Bis(silyloxy)enamines

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Introduction

N, N-Bis(silvloxy) enamines (BENA) (1), obtained by double silvlation of aliphatic nitro compounds,^{1,2} have been shown to serve as useful intermediates in organic synthesis owing to their ability to react both with nucleophiles and electrophiles.^{3,4} In the presence of fluoride ion, BENA behave as precursors of conjugated nitroso-

alkenes,3 which can be intercepted by various nucleophiles. On the other hand, BENA exhibit nucleophilic reactivity similar to that of enamines as demonstrated by reactions with carbocations generated from acetals and trimethylsilyl trifluoromethanesulfonate (TMSOTf).4

For systematic applications of its nucleophilic reactivity in organic synthesis, it is desirable to determine the range of electrophiles capable of reacting with BENA. Our approach is based on previous work of the München group which demonstrates that the reactions of carbocations with π -nucleophiles (alkenes, ^{5a-c} allylsilanes, ^{5a-c} silyl enol ethers,^{5d} silyl ketene acetals,^{5d} arenes,^{5e} metal- π -complexes^{5f,g}) and σ -nucleophiles (silanes, ^{5a-c} stannanes,^{5a-c} hydrocarbons,^{6a} amine boranes^{6b}) can be calculated by eq 1, where E = electrophilicity parameter,

$$\log k (20 \,^\circ\mathrm{C}) = s(E+N) \tag{1}$$

N = nucleophilicity parameter, and s = nucleophilespecific slope parameter (typically 0.6 < s < 1.2).

Since the nucleophile-specific slope parameters *s* have been found to be close to 1 for most π -nucleophiles,⁵ s can be neglected in semiquantitative considerations, and the strengths of electrophiles and nucleophiles are given by the E and N parameters, respectively. Thus, high values of *E* characterize strong electrophiles, and high values of N characterize strong nucleophiles.

Because of the availability of *E* parameters for numerous types of electrophiles, eq 1 would allow for calculation of the rates of their reactions with any nucleophile of known N and s parameters. We, therefore, investigated the kinetics of the reactions between BENA and benzhydryl cations. These data will then be used for the determination of *N* and *s* of these nucleophiles and finally the selection of electrophiles that are able to attack the BENA.

Results and Discussion

The benzhydryl cations were either synthesized and isolated as tetrafluoroborate salts (2a,b,c-BF₄) or generated in CH₂Cl₂ solution from the corresponding derivatives 2d-OAc, 2e-OSiMe₃, and 2f-Cl with TMSOTf. As shown in Scheme 1, the benzhydryl cations 2 attack the double bond of BENA 1 to give the N, N-bis(silyloxy)iminium ions 3. Subsequent fast desilylation furnishes the silyl nitronates 4 which are hydrolyzed upon aqueous workup affording the nitro compouds 5. The products 5 from the reactions of cations **2d**-**f** with BENA **1a**-**c** were isolated in 21-82% yield. We have not been able to isolate products from reactions with the amino-stabilized cations **2a**,**b**,**c**-BF₄, presumably because of the longer reaction times required for these electrophiles, during which decomposition of the silvl nitronates 4 may take place.⁷

The reactions of the cations **2a**-**f** with BENA **1a**-**c** exhibited second-order kinetics, first order with respect to 2 and 1 (Table 1). However, attempts to measure rate constants of the reactions of 1d with 2a,b,d-BF₄ in the absence of additives were unsuccessful because of fast polymerization of 1d, which can be explained by reaction of the phenyl-stabilized N.N-bis(silyloxy)iminium ion **3** $(\mathbf{R'} = \mathbf{Ph}, \mathbf{R''} = \mathbf{Me})$ with another molecule of BENA. The polymerization of BENA 1d can effectively be suppressed

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^{*a*} Ferrocenyl(phenyl)carbenium ion

Table 1. Rate Constants (20 °C) and Eyring Activation Parameters for the Reactions of BENA 1a-d with the Benzhydryl Cations 2a-f in CH₂Cl₂

BENA	cation	k_2 (20 °C), a L mol $^{-1}$ s $^{-1}$	$\Delta H^{\ddagger}_{,}$ kJ mol ⁻¹	ΔS , [‡] J mol ⁻¹ K ⁻¹
1a	2a	0.239		
	2b	6.94	39.6 ± 0.4	-93.7 ± 1.3
	2c	24.7	30.0 ± 0.7	-115.7 ± 2.6
	2d	42.2	33.3 ± 1.9	-99.9 ± 7.6
	2e	894	24.8 ± 1.5	-103.7 ± 6.2
	2f	$1.34 imes10^4$	20.6 ± 1.9	-95.6 ± 7.5
1b	2b	2.28	39.5 ± 1.4	-103.0 ± 5.3
	2c	10.5	31.8 ± 1.2	-116.9 ± 4.3
	2d	18.4		
1c	2c	4.10	37.7 ± 0.4	-104.6 ± 1.4
	2f	2278	22.6 ± 1.5	-103.6 ± 6.3
1d	2a	0.261		

 a If k_{2} has been measured at variable temperature, the entry in this column refers to the value derived from the Eyring equation.

by addition of tetrabutylammonium bromide which rapidly desilylates **3** to form the silyl nitronate **4** (R' = Ph, R" = Me) and bromotrimethylsilane. Since benzhydryl bromide **2a**-Br is more than 90% ionized under the conditions employed according to the carbocation absorbance at $\lambda = 625$ nm (20 °C, $[2a]_0 \approx 10^{-5}$ mol L⁻¹), the kinetics of the reaction of **2a** with **1d** can be measured in the presence of bromide ion (1.2 equiv with respect to **2a**). The propensity of the more electrophilic benzhydryl cations **2b**-**f** to form covalent benzhydryl bromides prevents analogous kinetic measurements of the reaction of **1d** with these carbenium ions. Variation of the benzhydrylium ions predominantly affects ΔH^{\ddagger} while ΔS^{\ddagger} remains around -100 J mol⁻¹ K⁻¹ as for reactions of other π -nucleophiles with terminal CC-double bonds.⁵

Figure 1 shows that rate constants (log k) determined for the reactions of **1a** with six benzhydrylium ions correlate linearly with their E parameters, indicating that eq 1 is suitable for describing these reactions. Slope and intercept of this correlation yield N(1a) = 4.76 and



Figure 1. Determination of the nucleophilicity parameters N and s for BENA **1a**-c [$E(2\mathbf{a}) = -5.53$, $E(2\mathbf{b}) = -3.85$, $E(2\mathbf{c}) = -3.14$, $E(2\mathbf{d}) = -2.64$, $E(2\mathbf{e}) = -1.36$, $E(2\mathbf{f}) = 0.00$]. For **1a**: N = 4.76, s = 0.86, r = 0.9983. For **1b**: N = 4.23, s = 0.93 (point in parentheses was not used for the correlation). For **1c**: N = 3.84, s = 0.87.

 $s(\mathbf{1a}) = 0.86$, i.e., the slope parameter *s* is of similar magnitude as for other π -nucleophiles with terminal double bonds.⁵ The closely similar slope parameters, reflected by the almost parallel graphs for **1a**, **1b**, and **1c** in Figure 1, indicate that the relative reactivities of these enamines are independent of the electrophilicity of the benzhydrylium ion. Assuming the same slope also for **1d** (*s* = 0.86), we can calculate *N*(**1d**) = 4.8 and compare the nucleophilic reactivities of **1a**-**d** with those of other π -systems.

As shown in Figure 2, the *N*,*N*-bis(silyloxy)enamines **1a**-**d** are approximately 9 orders of magnitude less reactive than typical enamines ($N \ge 11$), comparable to analogously substituted enol ethers and allylsilanes. The tremendous reduction of reactivity compared to other enamines can be explained by the electron-withdrawing inductive effect of the trimethylsilyloxy groups and the pyramidal geometry of nitrogen⁸ in BENA, which leads to a reduced n,π -conjugation between the nitrogen lone pair and the double bond.

While trimethylsilyl enol ethers and *tert*-butyldimethylsilyl enol ethers possess the same nucleophilicity,^{5d} compound **1b** was found to be two to three times less reactive than **1a**, possibly because the $n(N)-\pi(CC)$ interaction is reduced by the steric effect of the *tert*-butyl groups. The inductive effect of the ester group reduces the nucleophilic reactivity of **1c** by almost 1 order of magnitude compared to **1a**.

Surprisingly, the phenyl- and methyl-substituted compounds **1a** and **1d** show almost the same reactivity. We have previously discussed that the relative cationstabilizing effect of phenyl relative to methyl decreases

⁽⁸⁾ The barrier of nitrogen lone pair inversion of BENA varies from 50 to 60 kJ/mol depending on substituents: Dilman, A. D.; Tishkov, A. A.; Belyakov, P. A.; Ioffe, S. L. Unpublished results. Similar pyramidal arrangement of nitrogen in *N*,*N*-bis(silyloxy)aminobenzene has recently been reported: Dilman, A. D.; Lyapkalo, I. M.; Belyakov, P. A.; Ioffe, S. L.; Strelenko, Yu. A.; Tartakovsky, V. A. *Izv. Akad. Nauk, Ser. Khim.* **2000**, 1659–1660; *Russ. Chem. Bull. (Engl. Transl.)* **2000**, *49*, 1649–1650.



Figure 2. Nucleophilicity of BENA compared with other π -systems.

with decreasing electron demand.^{5d,9} While styrene is 10^3 times more reactive than propene, and α -methylstyrene is 20 times more reactive than isobutylene, α -(trimethylsilyloxy)styrene and 2-(trimethylsilyloxy)propene differ only by a factor of 6 in nucleophilic reactivity (Figure 2). Since the data in Figure 2 show that the electron-donating effect of the *N*,*N*-bis(silyloxy)amino group is somewhat weaker than that of a trimethylsilyloxy group, the unexpectedly low nucleophilicity of **1d** may be due to the fact that steric interactions between the phenyl and the *N*,*N*-bis(silyloxy)amino group inhibit both moieties to exert their full stabilizing effect.

In conclusion, the *N*,*N*-bis(silyloxy)enamines **1a**–**d** possess *N* parameters of 4–5, somewhat lower than those of structurally analogous silyl enol ethers. Following a previously formulated rule of thumb,^{5a–c} one can expect them to react with electrophiles (E > -9) at room temperature. While reactions with electrophiles of -5.5 < E < 0 have been observed under conditions of the kinetic experiments, the facile decomposition of the initially formed silyl nitronates had the consequence that products of electrophiles with E > -3 were employed.

Experimental Section

Kinetics. The rates of the reactions of benzhydryl cations **2a**-**f** with BENA **1a**-**d** were followed by UV-vis spectroscopy

Table 2.Second-Order Rate Constants k_2 of the
Reactions of theBis(2,3-dihydrobenzofuran-5-yl)carbenium Ion (2e-OTf)

with BENA 1a ^a (at $\lambda = 540$ nm, in Dichloromethane)						
<i>T</i> , °C	$[2e]_0$, mol L ⁻¹	$[1a]_0$, mol L ⁻¹	k_{2} , mol L ⁻¹ s ⁻¹			
-61.0	$2.102 imes 10^{-5}$	$7.536 imes10^{-4}$	14.8			
-50.9	$2.000 imes10^{-5}$	$3.983 imes10^{-4}$	24.1			
-39.8	$1.919 imes10^{-5}$	$3.822 imes10^{-4}$	45.2			
-29.5	$1.357 imes10^{-5}$	$4.151 imes10^{-4}$	102			
-29.5	$1.342 imes10^{-5}$	$4.104 imes10^{-4}$	97.4			
-18.7	$8.815 imes10^{-6}$	$2.654 imes10^{-4}$	167			

^{*a*} **2e**-OTf was generated in situ by adding 3-5 equiv of trimethylsilyl triflate to a dichloromethane solution of **2e**-OSiMe₃. Activated granulated 4 Å molecular sieves (0.6–0.8 g) were added.



Figure 3. Eyring plot and determination of the activation parameters ΔH^{\ddagger} and ΔS^{\ddagger} for the reaction of BENA **1a** with benzhydrylium cation **2e** (in dichloromethane, data from Table 2).

by using a working station similar to that described previously.¹⁰ UV–visible spectra in the range of 300–620 nm were collected as a function of time by the use of a J&M TIDAS diode array spectrophotometer interfaced with an IBM-compatible PC and controlled by Labcontrol Spectacle software (version 1.55). Measurements were made in Schlenk glassware and under exclusion of moisture by use of a Hellma 661.502-QX quartz Suprasil immersion probe (5 mm light path) equipped with a ground joint and fiber optic cables with standard SMA connectors. The temperature of solutions during kinetic studies was maintained to within ± 0.2 °C by using circulating bath cryostats (water–glycol bath for T > -10 °C, ethanol bath for T < -10 °C) and monitored with a thermocouple probe that was inserted into the reaction mixture.

Nucleophile concentrations $(10^{-4} \text{ to } 10^{-2} \text{ mol } L^{-1})$ considerably higher than cation concentrations $(10^{-6} \text{ to } 10^{-4} \text{ mol } L^{-1})$ were usually employed $([1]_0 \gg [2]_0)$, resulting in pseudo-first-order kinetics with an exponential decay of the benzhydryl cation concentration. Typical results of kinetic measurements at variable temperature are displayed in Table 2 and Figure 3. Further details can be found in the Supporting Information.

Chemicals. BENA **1a**, \mathbf{c}^{2a} and diarylmethyl compounds **2d**-OAc,¹¹ **2e**-OSiMe₃,¹² **2f**-Cl,¹³ and **2a**-**c**-BF₄¹² were synthesized according to literature procedures.

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BENA **1b** was synthesized according to a modified literature procedure.^{1b} To a solution of 2-nitropropane (135 μ L, 1.5 mmol) and NEt₃ (0.52 mL, 3.75 mmol) in CH₂Cl₂ (2 mL) at 0 °C was added *tert*-butyldimethylsilyl triflate (0.76 mL, 3.3 mmol), and the mixture was stirred for 3 h at 0 °C. A solution of citric acid (0.20 g, 1.0 mmol) and NEt₃ (0.83 mL, 6.0 mmol) in CH₂Cl₂ (2 mL) was rapidly injected. After 1 min, the mixture was diluted with petroleum ether (7 mL) and poured into H₂O (15 mL)/ petroleum ether (15 mL). The organic phase was washed with water (10 mL), saturated aqueous NaHCO₃ (10 mL), water (10 mL), and brine (10 mL) and dried (Na₂SO₄). Concentration in vacuo afforded 440 mg (ca. 90%) as a clear colorless oil containing 5–10% of Me₂-*t*-BuSiOH which can be removed by distillation. Bp 85–95 °C/0.03 Torr (Kugelrohr).

BENA 1d. Bromotrimethylsilane (0.58 mL, 4.4 mmol) was added to a solution of 1-phenylnitroethane (302 mg, 2.0 mmol) and NEt₃ (0.64 mL, 4.6 mmol) in CH_2Cl_2 (1.3 mL) at 0 °C, and the reaction mixture was kept at this temperature for 42 h. Then the mixture was diluted with petroleum ether (3 mL) and poured into H₂O (10 mL)/petroleum ether (5 mL). The organic phase was washed with aqueous NaHSO4·H2O (57 mg in 10 mL of water), water (2 \times 10 mL), and brine (10 mL) and dried (Na₂-SO₄). Concentration in vacuo afforded 520 mg (88%) of 1d as a clear colorless oil. Bp 120-125 °C (Kugelrohr)/0.038 Torr. 1H NMR (300 MHz, CDCl₃) $\delta = 0.16$ (s, 18H), 4.91 (s, 1H), 5.40 (s, 1H), 7.30-7.34 (m, 3H), 7.45-7.51 (m, 2H). ¹³C NMR (75.5 MHz, CDCl₃): $\delta = 0.1, 103.0, 127.8, 128.13, 128.07, 137.0, 159.1. ²⁹Si$ NMR (59.6 MHz, CDCl₃): $\delta = 24.6$ (SiMe₃). Anal. Calcd for C14H25NO2Si2 (295.53): C 56.90, H 8.53, N 4.74. Found: C 56.76, H 8.70, N 4.80.

Bis(p-methoxyphenyl)methyl Trimethylsilyl Ether (2f-**OSiMe₃**).¹⁴ To a solution of bis(*p*-methoxyphenyl)methanol (0.78 g, 3.2 mmol) and NEt₃ (0.58 mL, 4.16 mmol) in benzene (6 mL) at room temperature was added chlorotrimethylsilane (0.49 mL, 3.8 mmol), and the mixture was stirred at room temperature for 7 h. The reaction mixture was diluted with benzene and filtered, and the volatile components were evaporated. The residue was diluted with benzene, filtered, and concentrated in vacuo to give 886 mg (88%) 2f-OSiMe3 as a clear colorless oil. Bp 125-130 °C (bath temperature)/ 0.08 Torr, R₁(petroleum ether:ethyl acetate = 3:1) = 0.51. ¹H NMR (250 MHz, CDCl₃): $\delta = 0.06$ (s, 9H), 3.77 (s, 6H), 5.69 (s, 1H), 6.82, 7.22 (2d, J =8.5, 8H). ¹³C NMR (75.5 MHz, CDCl₃): $\delta = 0.2, 55.1, 75.6, 113.4,$ 127.6, 137.3, 158.5. ²⁹Si NMR (59.6 MHz, CDCl₃): $\delta = 17.80$ (SiMe₃). IR (KBr, cm⁻¹): 2955, 1611, 1511, 1302, 1249, 1171, 1073, 1037, 890, 841. Anal. Calcd for C18H24O3Si (316.48): C 68.31, H 7.64. Found: C 68.25, H 7.53.

4,4-Bis(p-methoxyphenyl)-2-nitrobutane. TMSOTf (114 μ L, 0.60 mmol) was added to a solution of **2f**-OSiMe₃ (158 mg, 0.51 mmol) and 2,6-di-tert-butyl-4-methylpyridine (5.1 mg, 0.025 mmol) in CH_2Cl_2 (1 mL) at -78 °C. Then, a solution of BENA 1a (0.55 mmol) in CH₂Cl₂ (1 mL) was added. After stirring for 15 min at -78 °C, the reaction mixture was quenched with a solution of BnNEt₃Cl (159 mg, 0.70 mmol) in CH₂Cl₂ (1 mL), kept for another 5 min at -78 °C, and treated with a mixture of AcOH (57 μ L, 1.00 mmol) and NEt₃ (153 μ L, 1.10 mmol) dissolved in CH₂Cl₂ (1 mL) followed by addition of AcOH (57 μ L, 1.00 mmol) in MeOH (1 mL). The cooling bath was removed, and the reaction mixture was allowed to warm to room temperature and kept at that temperature for an additional 1 h. For the workup, the mixture was poured into H₂O (10 mL)/Et₂O (20 mL). The organic phase was separated, and the aqueous phase was extracted with Et₂O (3 \times 10 mL). The combined organic extracts were washed with brine (10 mL), dried (Na₂SO₄), and concentrated in vacuo. Flash column chromatography (petroleum ether:ethyl acetate = 6:1) afforded 129 mg of a colorless oil (82%). R_{f} (petroleum ether:ethyl acetate = 3:1) = 0.41. Bp 140–150 °C (bath temperature)/0.03 Torr. ¹H NMR (250 MHz, CDCl₃): $\delta =$ 1.49 (d, J = 7.2, 3H), 2.28 (ddd, J = 5.3, 9.8, 14.5, 1H), 2.73 (ddd, J = 6.6, 8.5, 14.5, 1H), 3.72 (s, 3H), 3.73 (s, 3H), 3.81 (dd, J = 6.6, 9.8, 1H), 4.31–4.46 (m, 1H), 6.81, 6.82, 7.10, 7.12 (dd, J = 8.5, 8H). ¹³C NMR (62.9 MHz, CDCl₃): $\delta = 19.5, 41.2, 46.0, 55.2, 81.7, 114.0, 114.1, 128.3, 128.7, 135.1, 135.4, 158.2, 158.3. ¹⁴N NMR (21.7 MHz, CDCl₃): <math>\delta = 14.9, \Delta \nu_{1/2} = 470$ Hz (NO₂). IR (KBr, cm⁻¹): 2996, 2935, 2836, 1609, 1548, 1510, 1460, 1389, 1357, 1302, 1249, 1177, 1033, 827. Anal. Calcd for C₁₈H₂₁NO₄ (315.37): C 68.55, H 6.71, N 4.44. Found: C 68.64, H 6.89, N 4.81.

6,6-Bis(p-methoxyphenyl)-4-nitrohexanoic acid methyl ester was obtained from **1c** (0.55 mmol) and **2f**-OSiMe₃ (0.50 mmol) by the same procedure in 69% yield. Column chromatography: petroleum ether:ethyl acetate = 8:1, *R*/(petroleum ether: ethyl acetate = 3:1) = 0.22. Bp 205–210 °C (bath temperature)/ 0.09 Torr. ¹H NMR (300 MHz, CDCl₃): δ = 2.05–2.41 (m, 5H), 2.69 (ddd, *J* = 5.9, 9.6, 14.7, 1H), 3.62 (s, 3H), 3.74 (s, 3H), 3.76 (s, 3H), 3.80 (dd, *J* = 5.9, 10.7, 1H), 4.30–4.43 (m, 1H), 6.80, 6.84, 7.09, 7.10 (4d, *J* = 8.8, 8H). ¹³C NMR (75.5 MHz, CDCl₃): δ = 28.9, 29.9, 39.9, 46.0, 51.8, 55.2, 85.9, 114.0, 114.2, 128.2, 128.7, 134.6, 135.5, 158.2, 158.4, 172.0 (C=O). ¹⁴N NMR (21.7 MHz, CDCl₃): δ = 12.9, $\Delta \nu_{1/2}$ = 580 Hz (NO₂). IR (KBr, cm⁻¹): 2954, 2837, 1737, 1610, 1584, 1549, 1510, 1440, 1303, 1249, 1178, 1033, 830. Anal. Calcd for C₂₁H₂₅NO₆ (387.44): C 65.10, H 6.50, N 3.62. Found: C 65.16, H 6.34, N 3.48.

4,4-Bis(2,3-dihydrobenzofuran-5-yl)-2-nitrobutane. TM-SOTf (114 µL, 0.60 mmol) was added to a solution of 2e-OSiMe₃ (170 mg, 0.50 mmol) and 2,6-di-tert-butylpyridine (19 mg, 0.093 mmol) in CH₂Cl₂ (1.5 mL) at -60 °C. Then, a solution of BENA 1a (140 mg, 0.60 mmol) in CH₂Cl₂ (1.5 mL) was added. After stirring for 15 min at -60 °C, the reaction mixture was quenched with a solution of BnNEt₃Cl (159 mg, 0.70 mmol) in CH₂Cl₂ (1.5 mL), kept for another 5 min at -60 °C, and treated with a mixture of AcOH (57 μ L, 1.00 mmol) and NEt₃ (153 μ L, 1.10 mmol) dissolved in CH₂Cl₂ (1.5 mL) followed by addition of AcOH (57 μ L, 1.00 mmol) in MeOH (1.5 mL). The cooling bath was removed, and the reaction mixture was allowed to warm to room temperature and kept at that temperature an for additional 1 h. For the workup, the mixture was poured into H_2O (10 mL)/ Et₂O (20 mL). The organic phase was separated, and the aqueous phase was extracted with Et₂O (3 \times 10 mL). The combined organic extracts were washed with brine (10 mL), dried (Na₂- SO_4), and concentrated in vacuo. Flash column chromatography (petroleum ether:ethyl acetate = 8:1) afforded 36 mg of colorless oil (21%). $R_{\text{(petroleum ether:ethyl acetate = 3:1)} = 0.33$. ¹H NMR (300 MHz, CDCl₃): $\delta = 1.53$ (d, J = 6.6, 3H), 2.28 (ddd, J = 5.2, 9.6, 14.5, 1H), 2.73 (ddd, J = 6.5, 8.5, 14.5, 1H), 3.15 (td, J = 2.7, 8.5, 4H), 3.78 (dd, J = 6.5, 9.6, 1H), 4.36–4.48 (m, 1H), 4.53 (td, J = 2.7, 8.5, 4H), 6.70 (d, J = 8.2, 1H), 6.71 (d, J = 8.2, 1H), 6.91–7.04 (m, 4H). ¹³C NMR (75.5 MHz, CDCl₃): $\delta = 19.6, 29.7, 41.5, 46.5, 71.2, 81.7, 109.1, 109.3, 123.9, 124.3,$ 126.8, 127.1, 127.5, 127.6, 135.2, 135.5, 158.8, 158.9. IR (film, cm⁻¹): 2959, 2922, 2896, 1613, 1549, 1491, 1443, 1390, 1358, 1240, 1107, 983, 943, 818, 737. MS (EI): *m*/*z* (%) = 339 (14) [M⁺], 292 (11), 264 (14), 252 (20), 251 (100) [2e].

4-Ferrocenyl-4-phenyl-2-nitrobutane. TMSOTf (57 µL, 0.30 mmol) was added to a solution of 2d-OAc (0.10 g, 0.31 mmol) and 2,6-di-tert-butylpyridine (11.5 mg, 0.060 mmol) in CH₂Cl₂ (2 mL) at -78 °C. Then, a solution of BENA 1a (or 1b) (0.45 mmol) in CH₂Cl₂ (2 mL) was added. After stirring for 32 h at -78 °C (or 38 h for 1b), the reaction mixture was quenched with a solution of BnNEt₃Cl (96 mg, 0.42 mmol) in CH₂Cl₂ (1.5 mL), kept for another 5 min at -78 °C, and treated with a mixture of AcOH (52 µL, 0.90 mmol) and NEt₃ (167 µL, 1.20 mmol) dissolved in CH₂Cl₂ (1.5 mL) followed by addition of AcOH (52 μ L, 0.90 mmol) in MeOH (2 mL). The cooling bath was removed, and the reaction mixture was allowed to warm to room temperature and kept for an additional 1 h. For the workup, the mixture was poured into H₂O (10 mL)/Et₂O (20 mL). The organic phase was separated, and the aqueous phase was extracted with Et₂O (3 \times 10 mL). The combined organic extracts were washed with brine (10 mL), dried (Na₂SO₄), and concentrated in vacuo. Flash column chromatography on silica gel (petroleum ether:ethyl acetate = 20:1) afforded the product as a yellow oil in 31% yield from BENA 1a, 40% yield from BENA 1b. Two isomers in the ratio 2:1. R_{f} petroleum ether:ethyl acetate = 10:1) = 0.34. ¹H

⁽¹⁴⁾ For recent reports on the synthesis of trimethylsilyl ethers, see: (a) Gautret, P.; El-Ghammarti, S.; Legrand, A.; Couturier, D.; Rigo, B. *Synth. Commun.* **1996**, *26*, 707–713. (b) Karimi, B.; Golshani, B. *J. Org. Chem.* **2000**, *65*, 7228–7230.

NMR (300 MHz, CDCl₃): $\delta = 1.50$ (d, J = 6.7, 3H, minor), 1.55 (d, J = 6.6, 3H, major), 2.05 (ddd, J = 2.9, 12.3, 14.5, 1H, minor), 2.36 (ddd, J = 6.1, 8.1, 13.8, 1H, major), 2.65 (ddd, J = 6.1, 9.8, 113.8, 1H, major), 2.91 (ddd, J = 3.0, 11.1, 14.5, 1H, minor), 3.55-3.63 (m, PhČH of both isomers), 4.00 (s, 5H, major), 4.12 (s, 5H, minor), 3.92-3.98 and 4.03-4.21 (m, (CH)₄ of both isomers), 4.30-4.42 (m, CHNO2 of both isomers), 7.11-7.37 (m, 5H, Ph of both isomers). ¹³C NMR (75.5 MHz, CDCl₃): major, $\delta = 18.7$ (CHMe), 42.19, 42.7, 67.0, 67.17, 67.23, 68.0, 68.70, 81.3 81.8, 92.3, 127.0, 127.6, 128.69, 143.0; minor, $\delta = 20.5$, 42.15, 42.8, 65.9, 67.14, 67.7, 67.9, 68.74, 81.8, 92.3, 126.9, 127.7, 128.66, 143.6. IR (film, cm⁻¹): 3087, 3028, 2990, 2937, 1548, 1493, 1453, 1389, 1359, 1106, 1043, 1027, 1001, 860, 821, 731, 702. MS (EI): m/z (%) = 364 (20), 363 (88) [M⁺], 331 (30), 316 (18), 288 (16), 276 (25), 275 (100) [2d], 266 (14), 186 (15), 153 (24), 152 (19), 121 (37).

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Supporting Information Available: Concentrations and rate constants of the individual kinetic runs. This material is available free of charge via the Internet at http://pubs.acs.org.

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